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Evaluation of The Adsorption Capacity of The Expanded Perlite to Remove Linear Alkyl Benzene Sulphonic Acid (LABSA) from Aqueous Solution

D. Akin Sahbaz*[1], S. Balbay[2] and C. Acikgoz[3]

[1] Afyon Kocatepe University, Faculty of Engineering, Department of Chemical Engineering, TURKEY.
(E-mail: denizakin@aku.edu.tr)

[2, 3] Bilecik Şeyh Edebali University, Faculty of Engineering, Department of Chemical and Process Engineering, TURKEY.
(E-mail: senay.balbay@bilecik.edu.tr, caglayan.acikgoz@bilecik.edu.tr)

ABSTRACT

Linear alkyl benzene sulphonic acid (LABSA) is the major anionic surfactant material used in detergent formulations so that it is frequently present in domestic and civil wastewater. In this study, removal of LABSA has been carried out from its aqueous solutions by using the expanded perlite (EP) as potential adsorbent. Perlite products are made from an amorphous alumino-silicate rock, which has some very special properties: it contains water, which expands into steam on heating, producing a foamed structure. The EP particles used for adsorption process were in the range of 0.85-1.6 mm. Optimum parameters for the adsorption of LABSA over EP have been determined by studying the effect of pH, temperature, concentration of LABSA, amount of adsorbent and contact time. LABSA has been adsorbed over under batch measurements and adsorption process is monitored using UV spectrophotometer. The optimum pH value for adsorption capacity and removal efficiency of LABSA were 9.00 by (EP). The contact time of 3 hours was found to be sufficient to reach equilibrium, and so it was selected in further experiments. Thermodynamic parameters such as enthalpy change ($\Delta H°$), free energy change ($\Delta G°$) and entropy change ($\Delta S°$) were estimated. The experimental isotherm data were analyzed using Langmuir and Freundlich isotherm models. Experimental data were also evaluated in terms of kinetic characteristics of adsorption and it was found that the adsorption process obeyed the pseudo second order kinetic model. The present study has demonstrated that EP can be employed for the removal of LABSA from wastewater and potential as a cheap alternative to commercial adsorbents.

Keywords: Adsorption; Expanded perlite; LABSA.

5. INTRODUCTION

Adsorption technique using solid adsorbents is effective method for water decontamination. Most commercial systems currently use activated carbon [1,2] and polymer resins [3,4] as adsorbents to remove contaminants such as dyes and heavy metal ions in wastewater due to their high adsorption properties. However, they are quite expensive. In recent years, clay minerals such as zeolite, sepiolite, benzonite have been used to overcome the economic disadvantages of commercial adsorbents [5]. In this study we have selected perlite as an adsorbent to remove an anionic surfactant from aqueous solution.

Perlite, a glassy volcanic rock, can be expanded as much as 20 times its original volume when heated at 800-1200°C. Perlite is mainly composed of silicon (33.8 %), aluminium (7.2 %), potassium (3.5 %), sodium (3.4 %) and oxygen (47.5 %) [6]. Perlite as an adsorbent was investigated to remove of dyes such as Congo Red [7], C.I.

Basic Blue 41 [8], Methylene Blue [9], actinides such as thorium [10], and metal ions such as silver, copper, mercury [11,12] and arsenate [13]. However, a limited number of studies on the adsorption of surfactants by perlite have been found in the literature [14].

Surfactants, among which are the linear alkyl benzene sulphonic acid (LABSA), major constituents of household detergents including laundry powders, laundry liquids, dishwashing liquids and other household cleaners as well as in numerous industrial applications. The surfactants are responsible for foams in rivers and surface waters, thereby reducing the oxygen penetration in water and causing environmental risks for aquatic organisms [15]. They need to be removed from water to avoid environmental damages. Adsorption, which is a conventional method for surfactant removal from the water environment, has been studied extensively by using different adsorbents such as activated carbon [16], mineral oxides [17], polymer resins [18] and zeolite [15]. However, EP for the adsorption of surfactants is rarely reported.

In this study, the LABSA adsorption potential of EP from aqueous solutions has been studied. The effects of pH, adsorbent dosage, initial LABSA concentration, contact time and temperature on adsorption capacity of EP have been investigated. Also, this investigation aims to study kinetics and thermodynamic activation parameters to describe the rate and mechanism of adsorption.

2. MATERIAL AND METHODS

9.6. Preparation of adsorbent

The expanded perlite samples were provided from İzmir, Turkey. The samples were washed and filtered through a filter paper. The solid samples were dried at 110°C for 24 h. Then the dried perlite samples were mechanically sieved at different mesh numbers and segregated particles in the range of 0.85-1.6 mm to use in further experiments.

9.7. Batch experiments of LABSA adsorption

The adsorption of LABSA onto EP was carried out in a batch process by using 50 mL aqueous solutions of LABSA. The variable parameters were tested including pH of the initial solution, initial LABSA concentration, contact time and temperature. The pH value was adjusted by adding of dilute NaOH or HCl solution if necessary. All batch adsorption experiments were performed thermostat shaker with a shaking speed of 100 rpm. The LABSA concentration was measured using an ultraviolet spectrophotometer, JENWAY 7310, while the amount of LABSA adsorbed on EP (at a predetermined time t), q_t (in mg/g), was calculated through Eq. (1):

$$q_t = (C_0 - C_t)\frac{V}{W} \tag{1}$$

where C_0 is the initial concentration of LABSA (in mg/L), C_t (in mg/L) is the instant concentration of LABSA at a predetermined time t, V is the volume of the solution (in L), and W is the mass of EP (in g).

3. RESULTS AND DISCUSSION

3.1. Effect of pH

pH of aqueous solution was an important parameter that determined the adsorption capacity onto EP. The experiments were carried out in pH range 4-11 and the effects of initial pH on the adsorption capacities of LABSA on the EP were shown in Fig. 1. As can be seen, the adsorption capacity changed slightly from pH 4.0 to pH 8.0, then, increased largely when the pH value reached 9.0 and decreased largely when the pH value changed from pH 9.0 to pH 11.0.

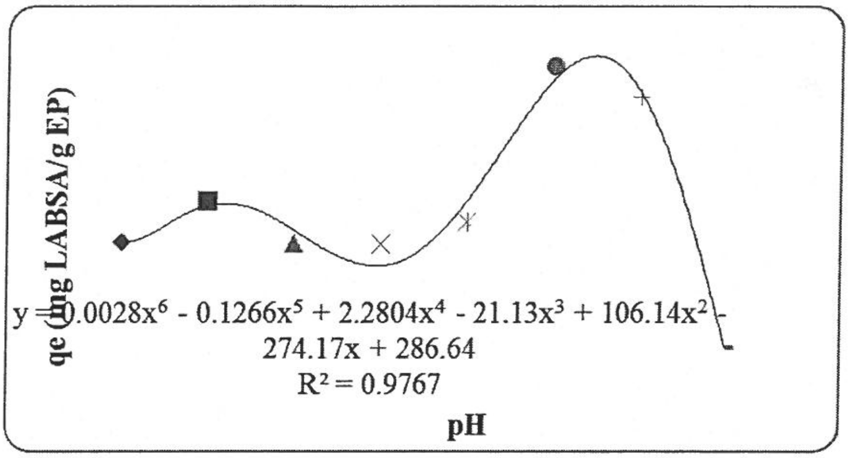


Figure 1. Effect of pH on the adsorption of LABSA onto EP (initial LABSA concentration: 60 mg/L, agitation speed:100 rpm, temperature: 15°C).

3.2. Effect of adsorbent dosage

Adsorbent dosage is an essential parameter which must be carefully adjusted during wastewater treatment. The effect of adsorbent dosage was investigated by varying the amount of adsorbent in the range of 0.1-0.5 g for 50 mL LABSA solution while keeping other parameters constant. As seen in Fig. 2, adsorption of LABSA increased by contact time and reached to a maximum value. The maximum amount adsorbed (q_e) decreased from 91.7 mg g^{-1} to 24.5 mg g^{-1} when the adsorbent dosage was increased from 2.0 g L^{-1} to 10.0 g L^{-1}. The decrease of adsorption was due to the concentration gradient between adsorbent and adsorptive [19].

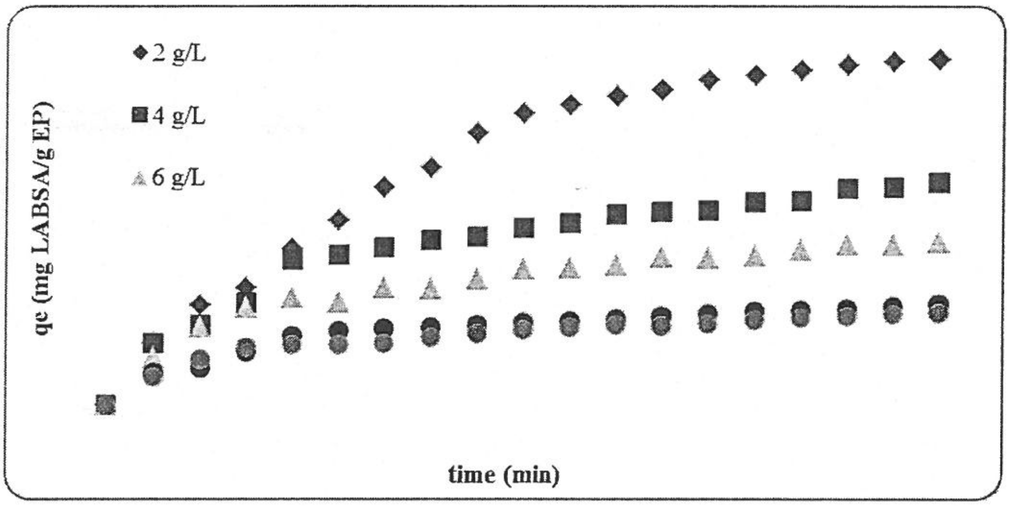


Figure 2. Effect of adsorbent dosage on the adsorption of LABSA onto EP (initial LABSA concentration: 300 mg/L, pH: 9, agitation speed:100 rpm, temperature: 15°C).

3.3. Effect of contact time and initial LABSA concentration

The experimental results of adsorption of LABSA onto EP at various concentrations with different contact time were shown in Fig. 3. The amount of LABSA adsorbed per unit mass of EP increased with an increase in the agitation time for any initial LABSA concentration and attained equilibrium within 3 h. Also, the adsorption amount of LABSA increased with the increase in the initial BB concentration. This was due to the increase in the driving force of the concentration gradient [20].

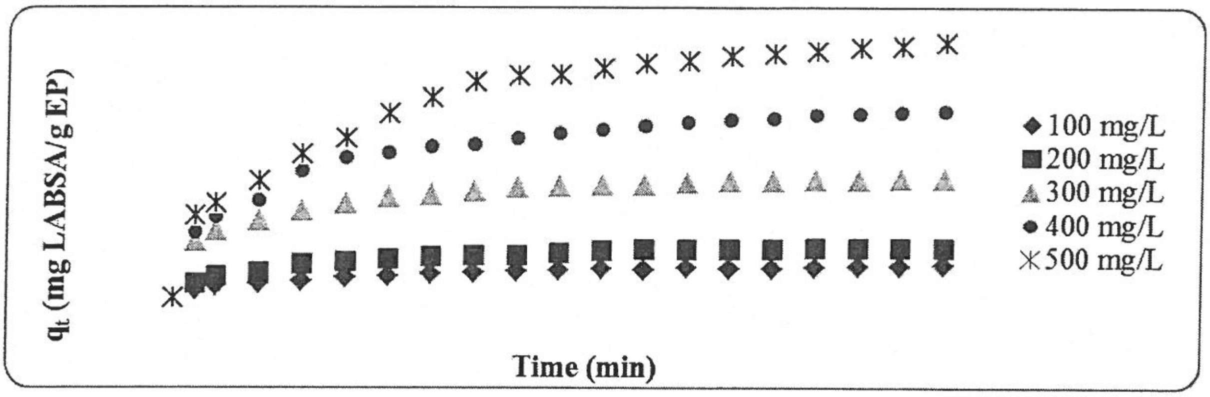


Figure 3. Effect of contact time and initial LABSA concentration on the adsorption of LABSA onto EP (EP: 2 g/L , pH: 9, agitation speed:100 rpm, temperature: 15°C).

3.4. Adsorption kinetics

The adsorption kinetics of LABSA onto EP are investigated with two kinetic models, namely the Lagergren pseudo first order and pseudo second order model.

The pseudo first order kinetic model can be expressed by the following equation [21]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

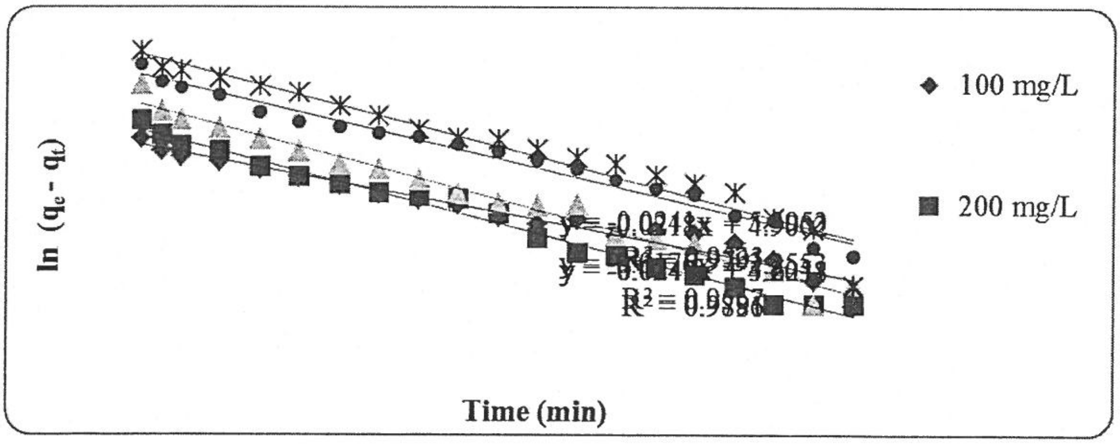
where q_e and q_t refer to the amount of LABSA adsorbed (mg/g) at equilibrium and at any time, t (min), respectively, and k_1 is the equilibrium rate constant of pseudo first order model (1/min). The plots of ln $(q_e - q_t)$ versus t were used to calculate the pseudo first order rate constant (Fig. 4 (a)).

The another kinetic model is pseudo second order model, which is expressed as [21]:

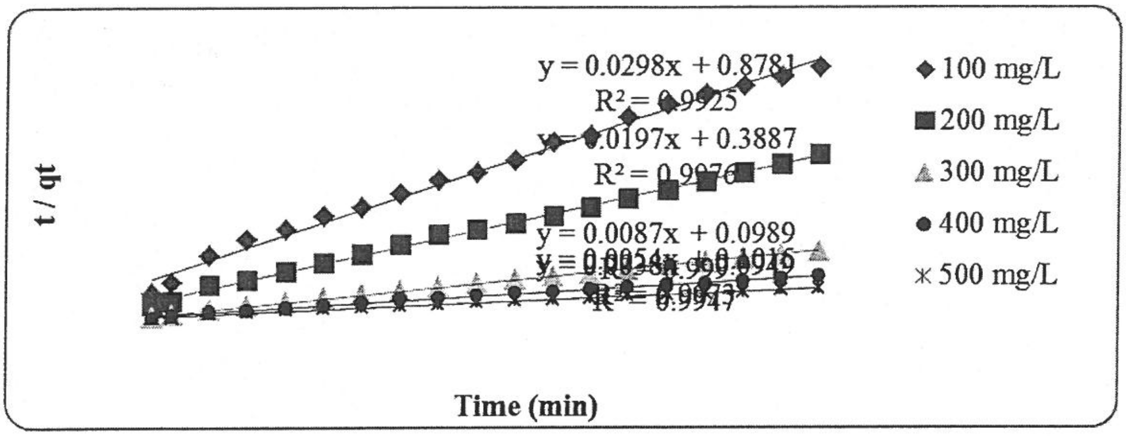
$$t / q_t = 1 / (k_2 \cdot q_e^2) + t / q_e \qquad (3)$$

where k_2 is the equilibrium rate constant of the pseudo second order adsorption model (g/mg.min). The plot of (t/q_t) versus t gives a straight line and q_e and k_2 values are calculated from the slope and the intercept, respectively (Fig. 4 (b)).

The corresponding kinetic parameters from both models for different initial LABSA concentrations are shown in Table 1. It was found that the correlation coefficient (R^2) for the pseudo first order adsorption model had low value (<97%) for LABSA concentrations studied and a very large difference existed between q (experimental) and q (calculated), indicating a poor pseudo first order fit to the experimental data. The correlation coefficient for the pseudo second order adsorption model had high value (>99%) for EP. Statistical analysis of the regression constants demonstrated that the adsorption kinetics of LABSA was more compatible with the pseudo second order model.



(a)



(b)

Figure 4. Kinetic models for LABSA adsorption onto EP for different initial LABSA concentrations: (a) Lagergren pseudo first order model and (b) pseudo second order model (EP: 2 g/L, pH: 9, agitation speed:100 rpm, temperature: 15°C).

Table 1. Parameters of the Lagergren first order and pseudo second order models for adsorption of LABSA onto EP.

Initial LABSA concentration (mg/L)	$q_{e,exp}$ *(mg/g)*	*Lagergren first order kinetic model*			*Pseudo second order kinetic model*		
		$q_{e,cal}$ *(mg/g)*	k_1 *(min⁻¹)*	R^2	$q_{e,cal}$ *(mg/g)*	k_2 $(_x10^3)$ *(g.mg⁻¹.min⁻¹)*	R^2
100	29.72	25.93	0.0176	0.9567	33.55	1.0113	0.9925
200	45.49	37.38	0.0243	0.9881	50.76	0.9984	0.9976
300	108.29	67.07	0.0247	0.9796	114.94	0.7653	0.9990
400	169.12	134.32	0.0218	0.9791	185.18	0.2873	0.9973
500	231.35	220.37	0.0241	0.9533	263.16	0.1522	0.9947

3.4. Adsorption isotherm models

The adsorption isotherm of LABSA on EP was measured under various initial LABSA concentrations. Langmuir and Freundlich isotherms were used to analyse the nature of adsorbate-adsorbent interaction.

Langmuir isotherm equation [22]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (4)$$

Freundlich isotherm equation [22]:

$$\ln q_e = \left(\frac{1}{n}\right)\ln C_e + \ln K_F \qquad (5)$$

where C_e is the equilibrium concentration of LABSA in solution (mg/L), q_e is the adsorbed value of LABSA at equilibrium concentration (mg/g), q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir binding constant, which is related to the energy of adsorption, K_F (mg/g $(L/mg)^{1/n}$) and n are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

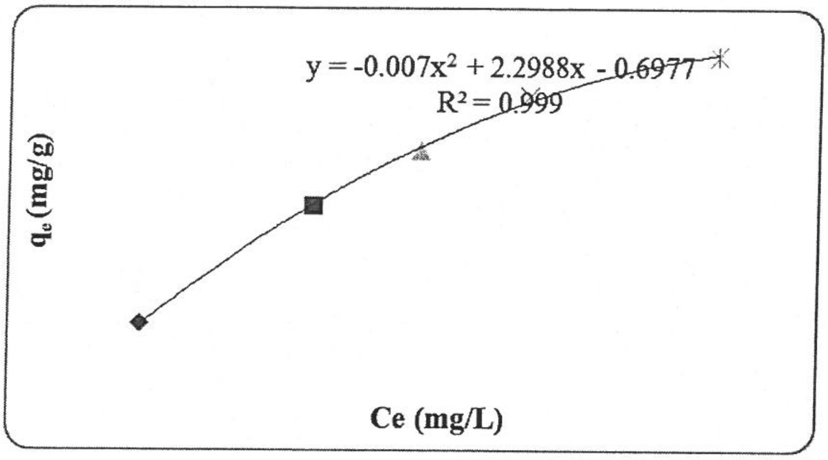
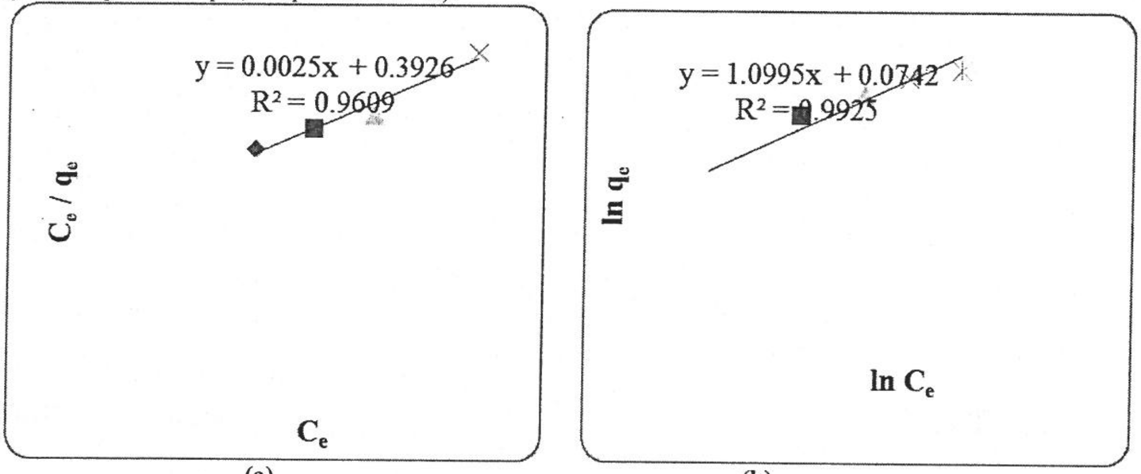


Figure 5. Adsorption isotherm of LABSA on EP (EP: 2 g/L, pH: 9, initial LABSA concentration: 200-500 mg/L, agitation speed:100 rpm, temperature: 15°C).



(a) (b)

Figure 6. Langmuir (a) and Freundlich (b) adsorption isotherms of LABSA on EP (EP: 2 g/L, pH: 9, initial LABSA concentration: 200-500 mg/L, agitation speed:100 rpm, temperature: 15°C).

Fig. 5-6 shows the adsorption isotherms of LABSA on EP and the calculated Freundlich and Langmuir isotherm constants are listed in Table 2. The correlation coefficients of Freundlich equation (0.9801) is higher than that of the Langmuir, which suggest that the adsorption takes place on heterogeneous surfaces of the EP with interaction between adsorbed LABSA molecules [23]. The Freundlich constant (1/n) for the EP adsorbents is smaller than 1, indicating a favorable process.

Table 2. Freundlich and Langmuir isotherm constants for the adsorption of LABSA on the EP.

Freundlich Adsorption Isotherm			*Langmuir Adsorption Isotherm*		
K_F [mg/g (L/g)$^{1/n}$]	*n*	R^2	q_m (mg/g)	K_L (L/mg)	R^2
6.32	1.439	0.9801	400	0.0064	0.9609

3.5. Effect of temperature and adsorption thermodynamics

To determine the effect of temperature on LABSA adsorption, adsorption experiment were also conducted at 288, 298, 308 and 318 K. The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be calculated by using the following Van't Hoff equation:

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

$$K_C = \frac{q_e}{C_e} \qquad (7)$$

$$\Delta G^{\circ} - \Delta H^{\circ} - T\Delta S^{\circ} \qquad (8)$$

where R is the universal gas constant (8.314 J/mol.K), T is the absolute temperature (in Kelvin) and K_C is the equilibrium constant. The value of ΔH° and ΔS° can be calculated from the slope and intercept of plots of ln Kc versus $1/T$ and are as shown in Fig. 7.

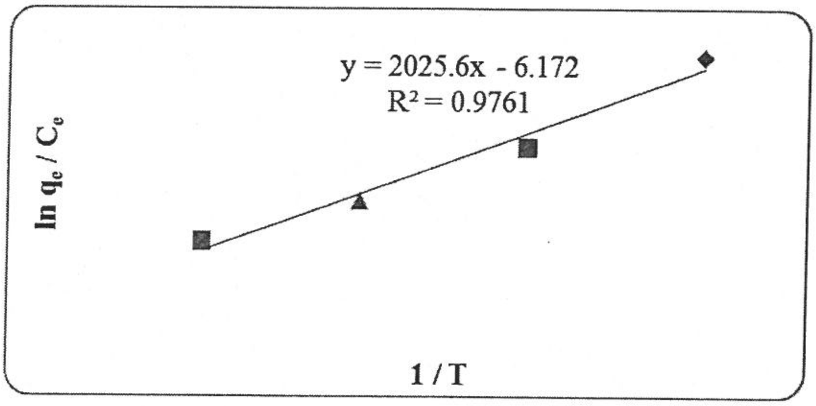


Figure 7. Van't Hoff plots for LABSA adsorption onto EP (EP: 2 g/L, pH: 9, initial LABSA concentration: 300 mg/L, agitation speed:100 rpm, temperature: 15-45°C).

The calculated thermodynamic parameters are given in Table 3. The negative value of ΔH° (-39.318 kJ/mol) shows exothermic nature of adsorption process, which is supported by the decreasing adsorption of LABSA with the increase in temperature. The value of ΔS° is found to be -142.39 J/mol.K for the adsorption of LABSA. The negative value of ΔS° suggest the decreased randomness at solid/solution interface during the adsorption of LABSA molecules onto EP [11]. The overall free energy changes during the adsorption process at 288, 298, 308 and 318 K was calculated using Eq. (8). The negative ΔG° values indicate that the adsorption is a spontaneous process, whereby no energy input from outside of the system is required. As the temperature increased from 288 to 318 K, the ΔG° values decreased, indicating less driving force and hence resulting in lesser adsorption capacity at higher temperatures [24].

Table 3. Thermodynamic parameters of LABSA adsorption by EP.

T (K)	*ΔG° (kJ.mol^{-1})*	*ΔH° (kJ.mol^{-1})*	*ΔS° (J.mol^{-1}.K^{-1})*
288	-2.063	-16.84	-51.31
298	-1.550		
308	-1.036		
318	-0.523		

4. CONCLUSION

The efficiency of the EP for the adsorption of LABSA from aqueous solution was investigated using batch adsorption technique under different experimental conditions. The results showed that the adsorption varied strongly by pH and temperature due to the change of critical micelle concentration of LABSA. A maximum adsorption capacity of 231.35 mg LABSA/g EP has been obtained for the initial LABSA concentration of 500 mg/L. Experimental results are in good agreement with Freundlich adsorption isotherm model. The pseudo second order rate equation described best the kinetic data of LABSA adsorption. The adsorption process was spontaneous and exothermic in nature.

This study showed that the EP has a high adsorption capacity to remove LABSA from aqueous solutions. Due to its low cost, it can be used as an influential adsorbent for the adsorption of LABSA from contaminated aqueous solutions.

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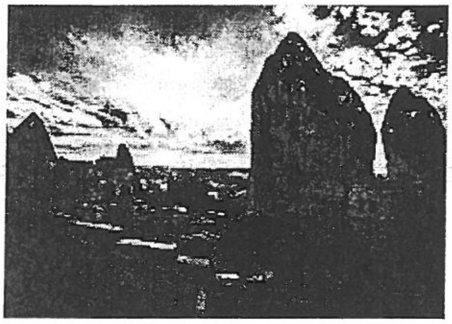
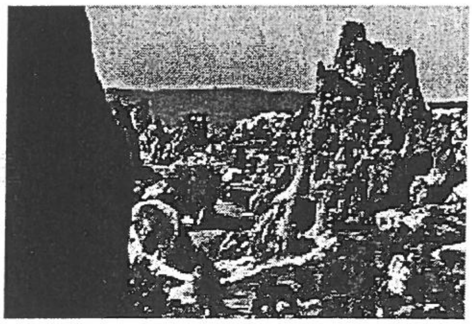
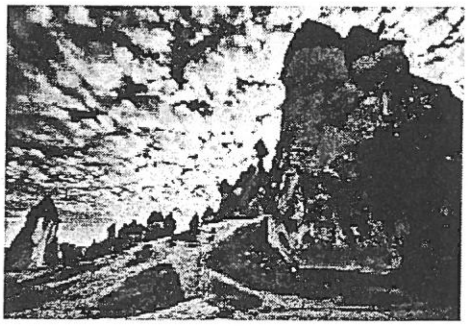






20 – 23 May 2015

Welcome to Cappadocia, Nevşehir

The idea of providing a scientific basis for discussing and solving, emerging problems in the fields of only environmental engineering such as water sources, pollution treatment technologies, aquatic life and etc. This idea initiated the first *"International Conference on Environmental Science & Technologies (Cappadocia, Turkey in 2013)"* that we also hosted and involved in the organization. However, environmental engineering is a whole with civil engineering in many countries in the World. Thus, basis idea of the second conference, which is named as ***International Conference on Civil and Environmental Engineering (ICOCEE)***, has been formed.

"International Conference on Civil and Environmental Engineering" will provide a comprehensive overview of effective strategies on the fields of civil and environmental engineering. Also, the ICOCEE conference will provide the opportunity to discuss and evaluate the solutions to the regional and global problems. All parties of civil and environmental engineering areas such as universities, industrial organizations, public institutions and organizations, local governments and legislators are welcome to attend to the conference in order to the share their experiences and to bring a common body of knowledge for the solutions of problems in the fields of civil and environmental engineering. The topics of the conference will include almost all areas of civil and environmental engineering.

Cappadocia (named as "*land of the beautiful horses*") is selected as the conference venue since it is one of the most fascinating and historical place in Turkey. It is also famed for its wine, valleys, underground cities, carved-from-rock churches & hotels, hot-air balloons, trekking and horseback riding tours. Owing to these prominent features of the place, participants will enjoy their stay besides benefiting from the conference.

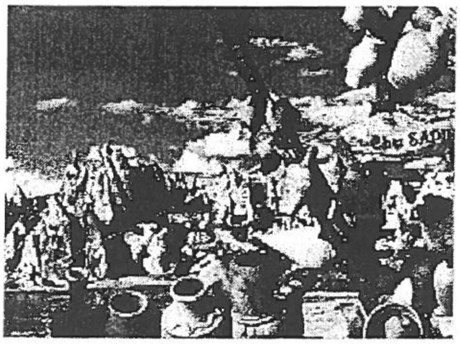
The four- day ICOCEE – Cappadocia'2015 conference that is going to be launched on May 20, 2015 in Cappadocia, Nevsehir, Turkey, provides a fruitful, international and unique forum for exchange of views among participants currently working in the areas of civil and environmental engineering.

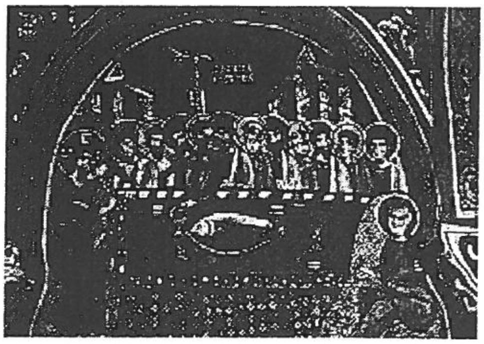
We hope you enjoy ICOCEE – Cappadocia'2015 conference and your stay in Cappadocia, Turkey.

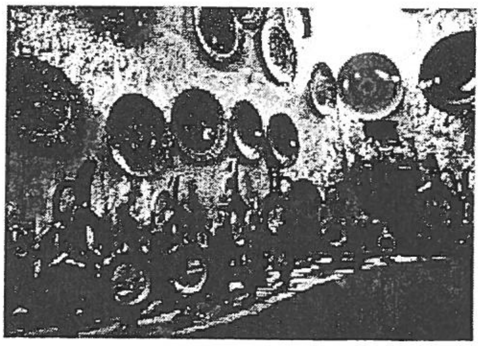
Conference Chairmen

Assoc. Prof. Dr. Serkan ŞAHİNKAYA

Assist. Prof. Dr. Erkan KALIPCI







Time	Thursday, 21 May 2015		
	Session 1 - A *Chair: Prof.Dr. Derin ORHON*	*Session 1 - B* *Chair: Assoc.Prof. Dr. Igor BODIK*	*Session 1 - C* *Chair: Prof. Dr. Magdaléna Bálintová*
09:00 - 09:15	S. Das, Y.P. Ting *Hydrogen peroxide aided sulphuric acid pre-treatment of electronic waste for improving gold recovery by metabolically-engineered strain of chromobacterium violaceum*	M. Balaban, D. Teresa Sponza *Treatment of olive mill wastewater by photooxidation to nano-ZnO-bentonite composite and recovery of OMW.*	E. Dorgeloh, D. Verschitz *European market for decentralized wastewater systems.*
09:15 - 09:30	D. Ulutaş, Z. Çokaygil, A. Özkan, Y.Güney, M.Banar *A new bitumen geosynthetic barrier mainly based on boron production waste clay for landfill liner systems.*	I. Bodík, T. Mackuak, M. Fáberová, M. Mosný *Occurrence of illicit drugs and pharmaceuticals in municipal wastewater and possibilities for their removal.*	I. Kocaturk, T.H. Erguder *Effect of influent COD/TAN ratio on carbon and nitrogen removal efficiency and stability of aerobic granules.*
09:30 - 09:45	M. Vekli, C.C. Çadır, F. Şahinkaya *Ground improvement via chrome and steel slags.*	Ş. Doğan, R. Kıdak *Efficiency of UV and UV/H_2O_2 processes for amoxicillin treatment.*	A. Bilgin *Investigation of nitrate treatment potential of tea waste.*
09:45 - 10:00	G.F. Gökçe, N. Mazlum, P. Hasanoğlu *Düzce potential investigation of domestic and industrial solid waste recoverable.*	R. Kıdak, Ş. Doğan *Flow reactor model for UV treatment of amoxicillin.*	M. Balintova, M. Holub *Adsorption of heavy metals from aqueous solution by non-modified clinoptilolite in fixed-bed system.*
10:00 - 10:15	Z. Bingül, F. Ekmekyapar Torun *Solid waste management in Erzurum.*	G. Doğdu, A. Yalçuk *Biosorption of commercial yellow 2G and indigo textile dyes by powder Hawaiian spirulina pacifica.*	E. Singovszka, M. Balintova *Cluster analysis of water quality in water reservoir Ruzin I., Slovakia.*
10:15 - 10:30	G. Demirel Bayık, A. Altın, Ö.F. Çapar *Effect of soil minerology on electrokinetic remediation.*	Ç. Ulusoy, D. Teresa Sponza *Removal of olive mill wastewater pollutants by UV and sunlight irradition with nano- SiO_2/Fe_3O_4 composite and reuse properties.*	K. Ashrafi, M. Zamani, G.R. Nabi Bid Hendi *Prediction of surface ozone concentration by a semi-empirical photochemical model.*
10:30 - 11:00	***Coffee Break***		
	Session 2 - A *Chair: Assist.Prof. Dr. Korkmaz BELLİTÜRK*	*Session 2 - B* *Chair: Assoc.Prof.Dr. Bülent İÇGEN*	*Session 2 - C* *Chair: Assist.Prof. Dr. Ece Ümmü DEVECİ*
11:00 - 11:15	K. Bellitürk, J.H. Görres, H.S. Turan, S. Göçmez, M.C. Bağdatlı, M. Eker, S. Aslan *Environmental quality of compost: Can composting earthworms (eisenia fetida) help manage compost nutrient ratios?*	D. Angın, G. Demir, S. Güneş, A. Ilci *Adsorption of orange 13 from aqueous solutions using activated carbon prepared from orange (citrus sinensis l.) pulp.*	O. Ayyildiz, B. Ileri, Ö. Apaydin *Reduction of nitrate by combined ultrasound and zero-valent magnesium under pH uncontrolled conditions.*

15:00 - 15:15	T. Akdeniz, H. Muhammetoğlu *Chlorine dosing management strategies for water utilities using GIS, SCADA and modelling tools: Case study of Yeşilbayir Antalya.*	I. Şentürk, H. Büyükgüngör *The effect of different pH at constant temperature on biohydrogen production from sewage sludge.*	A. Aygün, B. Nas, A. Berktay *Optimization of electrocoagulation process to treat young landfill leachate using response surface methodology.*
15:15 - 15:30	Ç.F. Karafakı *Water management policies in the European Union: Finnish integrated water management example.*	D. Akın Şahbaz, S. Balbay, C. Açıkgöz *Evaluation of the adsorption capacity of the expanded perlite to remove linear alkyl benzene sulphonic acid (LABSA) from aqueous solution.*	O. Tunç Dede *Evaluation of uncertainty for trace elements measurement in drinking water with ICP-MS.*
15:30 - 16:00		***Coffee Break***	
	Session 4 - A ***Chair: Assoc.Prof. Dr. Füsun EKMEKYAPAR***	***Session 4 - B*** ***Chair: Prof.Dr. Güleda ENGİN***	***Session 4 - C*** ***Chair: Prof. Dr. Gülfem BAKAN***
16:00 - 16:15	M.B.L.D. Diola, A.C. Resurreccion *Environmental contamination and residential exposure of mercury in artisanal gold mining area in Benguet, Philippines.*	D. Uçar, E. Çokgor, E. Şahinkaya, A. Yurtsever *Simultaneous nitrate and perchlorate reduction in elemental sulfur based autotrophic and heterotrophic processes.*	T. Tetik, Z. Celep *Structural performance of Sheikh Suleiman Masjid and its strengthening.*
16:15 - 16:30	Z. Maymekov, D. Sambaeva, J. Izakov, A. Isaev, J. Sydykov *Assessment of the cations and anions concentration distribution in underground potable waters, pH solution analysis subject to the temperature and content of technogenic sodium chloride.*	G. Güney, D. Teresa Sponza *Comparision of biological and advanced treatment processes for ciprofloxacin removal in raw hospital wastewaters.*	G. Bakan, S. Laçin *Environmental modeling approaches for exposure and risk assessment of prioritize chemicals in industries.*
16:30 - 16:45	C.R. Orozco, R.Q. Macasieb, B.J.M. Tapales, A.C. Resurreccion *Spatial variation and heavy metal concentration in sediments of Bued River: A preliminary assessment of a river nearby small-scale mining sites in the Philippines.*	P. Akan, M. Bekbölet *Adsorption and kinetic studies of molecular size fractions of humic acid onto anion-doped* TiO_2 *specimens.*	A. Kulig *From environmental audit of land to baseline report: Polish implementation of the EU directive on industrial emissions in the context of soil protection.*
16:45 - 17:00	B. Yalçın Çelik, K.O. Demirarslan *Eastern Black Sea region of domestic water capacity: The case of Artvin.*	Ö. Aktaş, Y. Toker, E. Şahinkaya *Biodegradation of various azo dyes in anaerobic batch reactors.*	G. Önkal Engin, M. Çelen *Land use change in İzmit Bay catchment.*
17:00 - 17:15	R. Çelik *Determination of Diyarbakır basalt aquifer water quality parameters and obtain thematic maps with using GIS technique.*	D. Karaeren, Z. Bozkuş *Comparison of performance of labyrinth and piano key weirs in increasing the spillway capacity of dams.*	E. Akçam, G. Bakan *Sediment and water pollution status of the mid-Black Sea coast of Turkey.*

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